

setzen Phenylhydrazin für die Titration frei. Auf diese Weise können p-Nitro-acetophenon oder o-Nitro-benzaldehyd neben Acetaldehyd bestimmt werden.

Experimentelles

Reagentien und Apparatur. 96%iges Äthanol, Eisessig p.a., konz. Salzsäure p.a., 0,2 N Kaliumbromatlösung, 0,1 N Jodlösung, Phenylhydrazin (wöchentlich frisch dest. und in dunkler Flasche aufbewahrt); Titri-pH-Meter (Radelkisz, Budapest), Platin- und Kalomel-Elektroden, Magnetrührer.

Bestimmung von p-Nitro-acetophenon. Etwa 0,1 g p-Nitro-acetophenon in 5 ml Äthanol unter Erwärmen im Wasserbad lösen, abkühlen, 6 Tr. (0,2–0,22 g) Phenylhydrazin und 3 Tr. Eisessig zusetzen und nach 10 min 50 ml Wasser und 8 ml konz. Salzsäure zufügen. Bei o-Nitro-benzaldehyd 10%ige Natriumchloridlösung anstelle von Wasser zur Herabsetzung der Löslichkeit des Phenylhydrazons anwenden. Anschließend mit 2 Tr. 0,1 N Jodlösung versetzen und mit 0,2 N KBrO₃-Lösung titrieren.

Das Ergebnis ist nach folgender Formel zu berechnen:

$$p\text{-Nitro-acetophenon } (\%) = \frac{[g_1/0,005407 - V] \cdot 0,0082575 \cdot 100}{g_2}$$

g_1 = eingewogenes Phenylhydrazin (g); g_2 = eingewogenes p-Nitro-acetophenon (g); V = verbrauchtes 0,2 N Kaliumbromat (ml).

Der Fehler der Bestimmung beträgt etwa 0,4%, die Standardabweichung 0,04 ml ±.

Literatur

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Oxidation of Thiourea by Potassium Dichromate

Oxydation von Thioharnstoff mit Kaliumdichromat

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Earlier work [1] on the oxidation of thiourea by dichromate refers to its oxidation to formamidine disulphide in which the authors have claimed quan-

Table. Determination of thiourea by dichromate
mEquiv. of dichromate taken = 2.415

Thiourea taken mMole	Dichromate consumed mEquiv.	Thiourea found mMole	% Error
0.1250	1.004	0.1255	+ 0.40
0.1250	0.9984	0.1248	- 0.16
0.1875	1.504	0.1880	+ 0.27
0.1875	1.502	0.1878	+ 0.16
0.2500	1.992	0.2490	- 0.39
0.2500	2.006	0.2508	+ 0.30

titative results. In this method, only one equivalent of oxidant is consumed by each mole of thiourea. However, it was found in the present study that this method does not yield exact results because the oxidation of thiourea proceeds slightly beyond the formation of formamidine disulphide. Quantitative oxidation of thiourea to sulphate could be effected by dichromate in sulphuric acid medium by boiling the solution for 10 min. In this way eight equivalents of oxidant are consumed by every mole of thiourea, thus enhancing the accuracy of the results by eight-fold. Ammonium ion and urea caused no interference. Thiocyanate was found to be oxidised to sulphate under these conditions. The method can be adapted for the determination of substituted thioureas provided the substituted groups are not attacked by the oxidant under the experimental conditions. Some typical results obtained for the determination of thiourea with dichromate are recorded in the Table. They are reproducible and accurate to within 0.5%.

Vanadate did not quantitatively oxidise thiourea to sulphate even in presence of common catalysts such as molybdate, silver sulphate and osmic acid.

Recommended Method. To a solution containing 0.1 to 0.3 mMole of thiourea, add 10 ml of 1:1 sulphuric acid. Dilute the mixture to about 50 ml and then add exactly 40 ml of 0.1 N potassium dichromate solution. Heat the mixture and boil for 10 min. Cool the mixture and titrate the remaining dichromate with standard 0.1 N ferrous ammonium sulphate solution using N-phenyl anthranilic acid as indicator. Run a blank under identical conditions without using thiourea.

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